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Multi-scale Computer Simulations to Study the Reaction Zone of Solid Explosives

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MULTI-SCALE COMPUTER SIMULATIONS TO STUDY THE REACTION ZONE OF SOLID EXPLOSIVES

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We have performed computer simulations at several different characteristic length scales to study the coupled mechanical, thermal, and chemical behavior of explosives under shock and other pressure loadings. Our objective is to describe the underlying physics and chemistry of the hot-spot theory for solid explosives, with enough detail to make quantitative predictions of the expected result from a given pressure loading.

INTRODUCTION

Several researchers[1-3] in the 1950's and 1960's, and others more recently[4, 5] have developed the fundamental picture that shock initiation in heterogeneous explosives is caused by the linking together of hot spots formed at inhomogeneities. Although there are exceptions, the hot spot picture is generally accepted as correct. Our work uses the computer hardware and software developed in the Advanced Simulation and Computing (ASC) program of the U.S. Department of Energy to explicitly include heterogeneities at the scale of the explosive grains and to calculate the consequences of realistic although approximate models of the coupled mechanical, chemical, and thermal behavior of explosives. Our simulations have been performed with ALE-3D, a three-dimensional, elastic-plastic-hydrodynamic Arbitrary Lagrange-Euler finite-difference program, which includes fully coupled chemical kinetics and heat transfer, and which is under development at this laboratory. These simulations have been performed at various characteristic lengths from nm scale, which resolves high-pressure flame fronts, to mm scale, which resolves continuum detonations.

Our objective is to describe the underlying physics and chemistry of the hot-spot theory for solid explosives, with enough detail to make quantitative predictions of the expected result from a given pressure loading. A multi-step reaction kinetics manifold is fundamental to our simulations. We develop complete equations of state and thermal transport properties for each of the species we identify. We present results for the explosive molecule HMX. We use three condensed-phase species, and two gas-phase species that are equilibrium mixtures. The first two reactions that connect the condensed species are endothermic, and the final two are exothermic, as described by Tarver and Tran[6] although our final reaction step is consistent with the quantum molecular dynamics (tight-binding with consistent charge) simulations of high-pressure high-temperature HMX decomposition by Manaa, et al.[7] The reaction zone is the sonic zone behind a leading shock in which pressure disturbances can influence the strength of the shock. In our studies, that zone also corresponds approximately to the zone in which the formation of gas product is complete.

Experimental results for shocks in several orientations of HMX single crystals have shown no initiation over a run distance of several mm for shocks that exceed the nominal Chapman-Jouget

detonation pressure.[8] As a result, we have focused on initiation of hot spots by the temperature localization that accompanies the shock driven collapse of material in the vicinity of a defect. We have calculated the ignition process near a defect when the flow stress of the HMX crystal is assumed rate-independent and isotropic. Simulations with rate-dependent plasticity of HMX shear planes are in process, and we will use them to help assess the effect of defect size on initiation threshold.

REACTIVE FLOW MODEL

The fundamental reactive flow model[9] is a rate law that describes the chemical change from the reactant, which is the unreacted solid explosive and binder, to product, which is a mixture of gases with, perhaps, some solid particulates such as graphite, diamond, and metal oxide. The rate law incorporates separate terms for ignition and growth to completion of the reaction. In some versions of the model, the ignition term is consistent with the idea of a shock wave collapsing gas-filled cavities (defects) and creating a localized hot spot. In other versions, it is consistent with the idea of localized shear bands creating hot surfaces. The growth to completion of reaction is consistent with the idea of a subsonic deflagration of the explosive moving from each hot spot outward. The surface area at the flame front increases as the deflagration proceeds outward from a localized hot spot. Eventually the flame fronts arising from multiple hot spots intersect, and the available surface area at the overall flame front decreases as the reaction completes. The changing surface area, which relates the mass rate of burning to the flame velocity, is represented by a form factor that depends on the extent of reaction. Although the flame velocity is very slow relative to the detonation velocity, it can result in complete transformation from reactant to product in the reaction zone (order mm) if the individual hot spots are very close together (order μm). In addition, there is a mixture rule to determine the equation of state of a mixture of partially reacted material that is present in the reaction zone. The mixture rule is, for many reactive flow models, a construction of additive volumes with pressure and temperature equilibrium enforced.[9] Other mixture rules may include a partial pressure construction[10] or adiabatic pressure equilibrium.[11-13]

Although such models are in general accord with the transformation of defects into hot spots, the coalescence of hot spots, and the subsequent detonation of the explosive, the parameter values are empirical fits to specific families of experiments. Previous model development has been focused on fitting families of experiments, using functional forms suggested by the experiments, and parameter fits to those experiments. Historically, the number of parameters has increased as each research group sought to include more and more families of experiments. This increase in complexity is not intrinsically bad, but requires each variation of explosive manufacture, age, and the temperature of the experiment to be treated as a new material, and subject to the same battery of experiments and parameter fitting. One outcome of our research is that we can identify some of the parameter values in the models with specific, measurable properties of the explosive. In this way, the models can be applied to a broader range of situations.

IGNITION MECHANISMS

Field[14] describes ten mechanisms for initiation in solid explosives that are predominantly thermal localization. Most of these are associated with inhomogeneities within the explosive crystal. Some, but not all explosive crystals also show ignition from shock waves in crystals without obvious defects. PETN (pentaerythritol tetranitrate) detonates for a shock stress above 9 GPa when the shock wave is normal to the (110) or (001) planes, but the threshold exceeds 19 GPa for shocks normal to the (100) or (101) planes.[15] Other explosive crystals, such as HMX, do not detonate even when the shock pressure exceeds the explosive detonation pressure.[8] For such explosives the presence of defects is required for initiation. In explosives that are nearly theoretical density, the average temperature behind a shock front is relatively low. Table 1 shows the temperature behind a shock front for our model of HMX starting at theoretical density as a function of shock pressure. In addition, we show the time to decompose HMX to 90% final product using our four-reaction five-species model based on Arrhenius kinetics. The first three reactions are identical to those of Tarver and Tran [6] and McClelland.[16] The final reaction uses the activation energy suggested by them, but with the

frequency factor adjusted to match the quantum molecular dynamics calculation of HMX decomposition reported by Manaa et. al.[7] The time to reaction is calculated assuming a constant pressure equal to the pressure of the incident shock. We observe that in our model, a defect-free crystal of HMX would not show transition to detonation at 40 GPa. As a consequence, defects are required to shock initiate HMX explosives at lower pressure.

TABLE 1. Calculated Shock Temperature and Time to 90% Decomposition for Full Density HMX

Stress, GPa	Temp, K	Time, sec
10	633	1.0×10^{6}
15	894	1.3×10^{5}
20	1196	2.6×10^{4}
25	1523	5.2×10^{3}
30	1885	6.2×10^{2}
35	2258	2.3×10^{1}
40	2653	2.6×10^{-2}

DEFECTS IN EXPLOSIVES

High-performance explosives are assemblies of organic crystals with bimodal (Figure 1) or trimodal size distribution. The separation for the peaks in the distribution is typically an order of magnitude or more, and the half-width of the lognormal distribution is typically between 2x and 3x the diameter of the mean. Defects within the larger explosive crystals can be visualized and quantified by immersion in an index-of-refraction matching fluid and viewing with an optical microscope. However, the defects within HMX, RDX, and CL-20 crystals, make up between 0.2% and 1.0% of the volume of the organic crystal as measured by the column gradient method.[17, 18] We conclude that most of the gas-filled void of the PBX after pressing, typically 2% to 4% of the volume, is intra-granular porosity. One possible manifestation of this porosity is that surface irregularities may be incompletely wetted and filled by the plastic binder. These irregularities may be caused either by grinding or steps in the crystal growth. We are at present trying to determine the gas-filled void size and morphology in PBX.

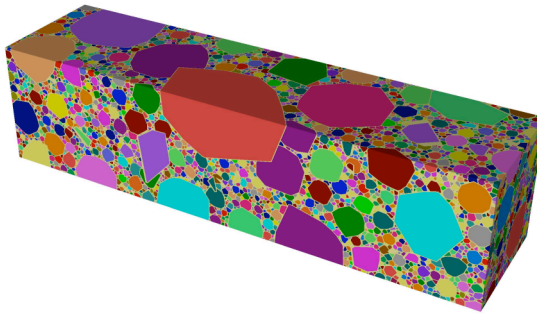

FIGURE 1. Bimodal assembly of HMX crystals

It has been recognized that if the defect and the subsequent hot spot is too small, thermal conduction to the surrounding cooler crystal will remove heat from the hot spot faster than continued decomposition can replenish it[1, 19]. As a result, there is a minimum size below which the gas-filled volume does not contribute to shock initiation. We have simulated the evolution of a spherical volume of explosive products in HMX at the nominal flame temperature. The critical hot spot size depends on the pressure and temperature of the unreacted material that surrounds the hot spot (Figure 2). At 2.5 GPa, the calculated critical spot diameter is 0.25 ± 0.05 μm for both 20 and 80 °C. At 10 GPa, the critical diameter is 0.17 ± 0.03 μm at 20 °C and 0.08 ± 0.02 μm at 360 °C. These diameters are significantly larger than the results reported by Tarver et. al.[19] as a result of the pressure dependent transport properties used in this work. At 10 GPa, our conductivity for the unreacted HMX is twice that used by Tarver, and our conductivity for the gas products is 20 times the nominal low-pressure value. The critical hot spot sizes we calculate are too small for easy detection by optical microscopy, but too large for reliable resolution by Small Angle X-ray Scattering techniques.

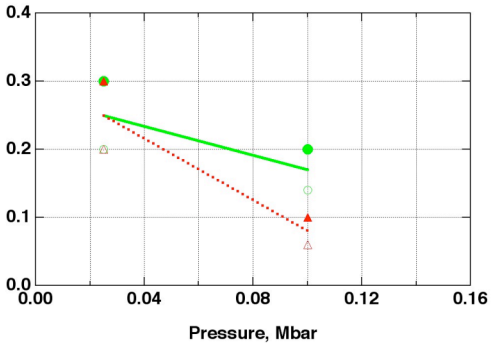

FIGURE 2. Calculated critical hot spot diameter, µm, at 2.5 and 10 GPa for room temperature and shock temperature.

IGNITION NEAR A DEFECT

The collapse of a void is fundamentally different when the shock front is narrow relative to the void dimension, as compared to collapse by a shock front that is broad relative to the void dimension. We constructed assemblies of explosive particles and binder at theoretical density to examine the structure of a shock after passage through such an assembly. If the stress wave is averaged over a macroscopic plane, the response is a notably longer rise time. This is caused by a statistical distribution of arrival times over the given test plane. At a specific location in that plane, the arrival time depends on the relative amount of binder and crystal that the shock has traversed. When the shock has progressed far enough through the assembly, the statistical distribution becomes steady. On the scale of the void, however, the shock is narrow. As a result, void collapse is not well described by a spherically symmetric, quasi-static compression, but by an unsymmetrical collapse from a sharp shock. Experiments and computer simulations of the collapse of simple geometric shapes (cylinders, spheres and cones) by sharp shocks[14, 20-23] have illustrated the asymmetric collapse of the void, and the localization of temperature in the gas-filled cavity and in the material surrounding the void.

Accurate simulations of this ignition process have proven difficult. Our use of Arrhenius kinetics to describe the decomposition chemistry, even with greatly simplified kinetic schemes, shows a characteristic sensitivity to temperature. The advection step taken in either ALE or Eulerian computer simulation program frameworks mixes hot gas products with cooler reactants. Parameter values and choices of sub-models for mixing that have been determined to work best for hydrodynamic simulations over the years are not necessarily the optimum choices when chemical kinetic rates must be calculated. Our results for this aspect of shock initiation must be considered preliminary.

We do, however, obtain the realistic result that the same cavity filled with an organic liquid (for example a solvent pocket) is much less apt to ignite for a given shock stress. Our simulations assume a regular defect geometry, although defects between grains in a PBX assembly are never regular. As a result, the irregularities of the cavity will be reflected in irregularities in the temperature field that results from cavity collapse. The chemical kinetic rates will emphasize the hottest spot consistent with the dimensional requirement for sustained growth of reaction. Second, our simulations have used a von Mises plasticity model, which collapses the spherical cavity symmetrically. In the literature, the constitutive model of the reactant is either taken to be von Mises plasticity or viscosity, which results in similarly symmetric collapse, although with a size dependence not seen with rate-independent plasticity. For these organic crystals, however, slip on a few planes is favored over most other planes. We have begun to examine the collapse of a spherical void with such a plasticity model. It is still over-simplified, but illustrates that the subsequent collapse of the cavity is not symmetric, and so leads to further temperature localization. The coupling of this plasticity model with the reaction chemistry is still in progress.

HIGH-PRESSURE FLAME PROPAGATION

In the standard view of reactive flow modeling, isolated hot spots connect with each other by deflagration to form a volume of hot products. The deflagration fronts move through the unreacted solid with a velocity that depends on pressure and temperature. We use direct numerical simulation to calculate the velocity of the deflagration. In order to simulate deflagrations at high pressure, we need complete equations of state of the various species involved, thermal transport properties of the species, and the chemical reaction kinetic rates embedded in a computer simulation program. At

high pressure, greater than 1 GPa, species diffusion is inhibited relative to thermal diffusion.

We used the thermochemical equilibrium computer programs CHEQ[24] and Cheetah[25] to calculate enough points on the equation of state surface to construct a tabular equation of state in one of this laboratory's standard formats (LEOS). Historically, such thermochemical codes were unreliable estimates of states far removed from the Chapman-Jouget (CJ) adiabat. They were tuned to obtain reliable estimates of detonation properties for CHNO explosives using equation of state forms with few adjustable parameters, and with a concomitantly limited range of validity. More realistic exponential-6 molecular potentials that are now in use have been calibrated with high-pressure experiments on various molecules that are found in the decomposition products.[25] These calibrated potentials have led to improved fidelity over a wide range of temperature and density.

Calculation of flame advance also requires knowledge of the transport properties. Bastea[26] has modified Enskog theory to obtain thermal conductivity consistent with the mixture of spheres represented by the exponential-6 potentials. The values he calculates at high pressure are typically within a factor of two or so of earlier estimates we made using Bridgman's model for high-density fluids. For future work in this and other related research, Bastea has also calculated consistent viscosity and species diffusivity.

To the extent that the deflagration rates are subsonic, the formulation of the numerical problem could be cast as quasi-static. However, at the small mesh size needed to resolve the deflagration front (order 0.5 nm), the stable time step for explicit finite-difference calculation of heat transfer is comparable to the stable time step for explicit finite-difference calculation of compressible hydrodynamics. As a result, it is numerically efficient to calculate the compressible flow dynamically. Results of such simulations at lower pressure, including assessment of the effect of various properties on the calculated deflagration speed were presented previously.[27]

Our computer simulations are in reasonable agreement with reaction front propagation measurements made by Zaug[28] on both pure HMX and LX04, which contains 15% Viton A binder by weight (Figure 3). In addition, our results show that the velocity decreases at pressures greater than 20 GPa. The experimental results are consistent with that decrease. In our constant pressure simulations, the flame temperature begins to decrease with increasing pressure at about 20 GPa. We calculate the temperature of an isobaric flame by calculating the enthalpy of the solid reactant. Although the analytic functions we routinely use for solids require a constant specific heat, which is not accurate, the error in the entropy is small because the thermal contribution is small at high pressure. The tabular equation of state can then be interrogated at constant pressure and enthalpy to obtain the flame temperature.

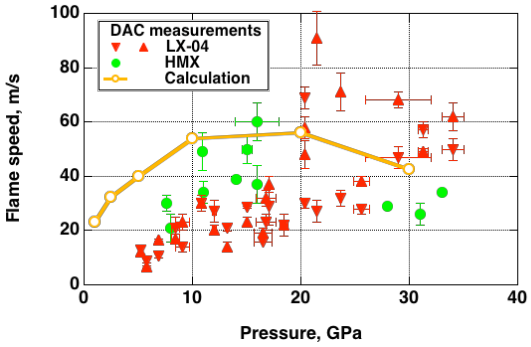

FIGURE 3. Calculated and measured flame speed in m/s, as a function of pressure

Our computed flame thickness (Figure 4) decreases with pressure, principally caused by the increased density of the compressible gas products at high pressure.[27] We have also calculated the flame propagation speed as a function of pressure when the reactants are at the temperature of a shock in unreacted HMX. Although our temperature estimate of shocked but unreacted HMX is crude, the significant speed-up in flame propagation is realistic. Over the pressure range from 1 to 30 GPa, the flame speed we calculate into material heated to the temperatures given in Table 1 is

$$v = v_0 p^n \qquad (1)$$

where v_0 is the flame speed at 1 GPa, and p is the shock pressure in GPa. From our calculations v_0 is 22 and n is 0.5

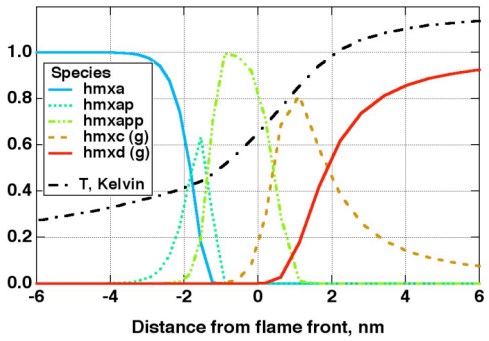

FIGURE 4. Calculated species concentration (mass fraction) and Temperature (in units of 2500K) profiles for a flame propagating steadily at 2.5 GPa.

GROWTH OF REACTION

When the hot spots are isolated, for example a regular cubic array of hot spots, the initial behavior has precisely the same functional form as does the single void,

$$\frac{dF}{dt} = f_v^{1/3}\frac{3}{r_0}vF^{2/3} \qquad (2)$$

Here F is the mass fraction of explosive consumed, f_v is the volume fraction of defects, and also the volume fraction of hot spots, which is assumed the same, and r_0 is the radius of the hot spots. When the hot spot centroids are located randomly, with no special care taken to forbid the overlap of neighbors, some hot spots will overlap from the beginning. As a result, the surface to volume ratio will increase over that of isolated spheres, so that the initial rate will be somewhat higher and the power law a will no longer be 2/3. For random arrays of hot spots, we rely on numerical simulations and fit the results to simple functional forms. We performed a family of simulations of the deflagration of clusters of hot spots varying the initial hot spot volume fraction, diameter, and the deflagration velocity. The results of those simulations can be represented by

$$\frac{dF}{dt} = Af_v^{1/3}\frac{3}{r_0}vF^a(1-F)^b, \qquad (3)$$

where the prefactor A changes with the values of a and b. From our simulations, a is 0.63, b is 0.70 and A is 1.04.

APPLICATION OF THE CONTINUUM MODEL

We used approximately 7-diameter long explosive cylinders as our computational acceptor charges, which varied between 1 and 6 mm diameter. The donor charges were all 10 mm long, and had the same diameter as the acceptor charge, and were detonated as an ideal explosive. As a result, the acceptor charges are overdriven. We observed computationally that for those diameters in which a detonation propagated, the propagation speed decreased down the length of the charge and reached a steady value within 4 or 5 diameters of propagation. In all simulations, the radial and axial zone size was the same, 0.02 mm. Tarver and we confirmed that the results do not change when 0.01 mm zones were used. The increase in detonation speed with increasing charge diameter is in substantial agreement with the experiments performed at LANL by Campbell and Engelke.[29] The volume fraction of hot spots is taken to be the void fraction of PBX-9404, f_v=0.015, which we obtain from the ratio of the theoretical maximum density (TMD) of the explosive to the measured density. From the comparison of our simulations to the experiments, the characteristic defect has approximately 1μm diameter(Figure 5). For these simulations, we used both the ignition term described by Tarver[30] and an ignition term constructed from the results of our simulations of the growth of reaction near a defect using von Mises plasticity theory.[31] For these simulations of an overdriven detonation propagating to steady state, the results are not sensitive to the ignition term.

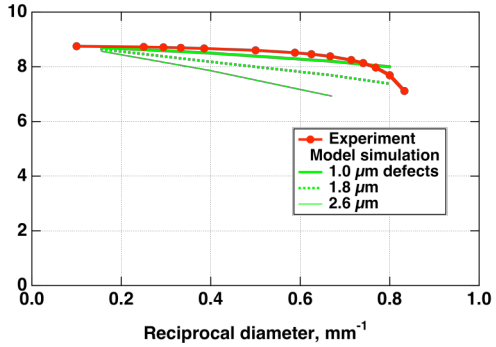

FIGURE 5. Calculated detonation speed (km/s) as a function of inverse diameter of unsheathed rate sticks of PBX-9404.

We also observed in our simulations of flame propagation that if the pressure were reduced on the hot product gases, the flame did not slow to the value that corresponded to the new pressure, but instead died out and stopped. We observed that this phenomenon occurred even with a relatively slow pressure reduction, so long as the reduction were fast enough that hot gases evolving from the flame front could not replenish the temperature of the adjacent gas, which was reduced by the adiabatic expansion to lower pressure. This observation is not unique to our simulations. It is a well known and widely utilized technique in the rocket motor industry that emergency abort of a solid propellant rocket motor is accomplished by reducing the pressure in the combustion chamber, frequently by applying linear shaped charges to burst the motor case. As a result, however, we reasoned that the use of experimental results on thin pulse initiation and initiation failure could be used to also infer the characteristic dimension of hot spots. If the pulse is so thin that the flames propagating from each of the hot spots do not coalesce before the rarefaction drops the pressure and temperature of the gas products, then a detonation will not propagate. If, instead, the pulse duration is longer than that, then the flames can coalesce, increasing the pressure behind the shock front, and accelerating the reactive front to a full detonation.

Weingart, et. al.[32] summarize the thin-pulse initiation studies their own, as well as those of Gittings[33] and Trott and Jung[34] in PBX-9404. The data are reasonably well fit by

$$P^2\tau = 5.5 \tag{4}$$

where P is the shock stress in GPa and τ is the pulse duration in μs for pulse durations between 5 ns and 1 μs. we assume that the average separation of potential hot spots, δ, is based on the characteristic hot spot radius, r_0, and is given by

$$\delta = \left(\frac{4\pi}{3f_v}\right)^{1/3} r_0, \tag{5}$$

and the unburned web separating two adjacent hot spots is given by $\delta - 2r_0$. This distance, l_0, is foreshortened in the direction of propagation behind a shock wave with stress, P, by the density increase. For shocks in unreacted HMX, the relative volume, V, behind a shock in the range of 2 to 30 GPa is approximately

$$V = V_0 P^{-0.124} \tag{6}$$

where V_0 is the relative volume at 1 GPa, 0.985. The time available for two deflagrations to meet at the center of the unburned web is then given by

$$\tau = \frac{Vl_0}{2v}, \tag{7}$$

where v is given by Eq. (1). Whether we use the criterion of Eq. (4) or the critical energy criterion proposed by Walker and Wasley[35] and fit to the same data,[33] we infer a similar characteristic dimension as a function of shock pressure as given in Table 2. At the highest pressure shown in the table, 30 GPa, we infer a characteristic dimension for the hot spots of 1 μm diameter, similar to that we inferred from the rate-stick experiments with a 37 GPa detonation pressure.

Table 2. Characteristic radius, r_0, inferred from thin pulse experiments on PBX-9404 using Eq. 4 (τ_1) or critical energy (τ_2).

Stress, GPa	τ_1, μs	r_{01}, μm	τ_2, μs	r_{02}, μm
10	0.055	2.6	0.043	2.0
20	0.014	0.98	0.014	0.98
30	0.006	0.56	0.007	0.64

IMPLICATION FOR CONTINUUM MODELS AND FUTURE WORK

We have shown that our detailed analysis of hot spots that link up by the propagation of flames, and our calculated flame velocity as a function of pressure and reactant temperature can be used to infer a consistent picture of shock initiation and detonation. The characteristic diameter of hot spots (and the defects that trigger them) in PBX-9404 is 1 μm. This is a size that is comfortably larger than the minimum hot spot size that will propagate. It is, however, a difficult size to measure independently. Perhaps even more importantly to the propagation (or decay) of thin pulses or otherwise attenuating shocks is the observation that pressure decay in the reaction zone will result in the flames going out, not just slowing down. This will necessarily complicate the model, because the flame propagation velocity is not simply a function of the current pressure, but rather depends on the history of the pressure and flame temperature.

The importance of this observation is that a continuum model based on the current pressure is by necessity a compromise. Tarver[30] noted that the same model parameter values cannot be used to

represent initiation from thin pulses and the behavior of propagating detonations. We anticipate that a more complex model that incorporates the idea that the reduction of a flame temperature will stop a reactive shock will be required to represent both these two conditions, as well as initiation from diverging shocks.

ACKNOWLEDGEMENTS

This research has enjoyed the enthusiastic support of Randy Simpson, who was the leader for explosive research in both ASC and the Munitions Technology Development Program, during this project's start, and has remained a staunch supporter throughout its life. Stew Keeton, Estella McGuire and Tom Reitter performed many of the numerical simulations for this project, using state-of-the-art computer hardware (that was sometimes being beta-tested by them) to do large scale computing. The ALE-3D team, under the leadership of Richard Sharp, has supported this work by modifications, improvements, and the addition of new features to their simulation program. Of that team, we especially want to recognize several individuals. Gary Friedman created dramatic improvements in the efficiency of generating shapes, programmed the algorithms for several of the early methods of developing shapes, and served as the point of contact and interface between this project and the team; Al Nichols was responsible for the chemistry, deflagration, and heat-transfer modules in ALE-3D and frequently repaired our input files that attempted to use those modules. Rich Becker and Nathan Barton provided their models for crystal plasticity and examples as well as advice on their use. Bob Cooper, Andy Anderson, Brad Wallin, Rob Neely, and Scott Futral were also instrumental in making our progress possible.

In addition, Sorin Bastea provided equations of state for intermediate and final decomposition products with CHEQ and Cheetah, and also developed methods to calculate consistent transport properties for the explosive products. Riad Manaa's Quantum Molecular Dynamics simulations of the decomposition of HMX at high temperature and pressure have given us a benchmark for testing our simplified chemical kinetics reaction scheme at high pressure and temperature. Craig Tarver provided his unpublished parameters for reactive flow modeling of PBX-9404 in small diameter charges, and freely shared his expertise in applying reactive flow models to calculations of macro-scale phenomena. Ed Lee provided a willing ear and the voice of reason for most of our nascent ideas. A number of extended discussions with Ralph Menikoff, LANL, have provided us with an alternative point of view on cavity collapse. His thoughtful comments have been very helpful to us in analyzing our results.

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